GLASS COMPOSITION

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a glass composition.

2. Description of the Related Art

[0002] A glass composition is generally used in various applications as glass products by heating various salts, oxides, or the like such as inorganic minerals as raw materials to high temperatures for forming molten glass, deaerating gas generated through a reaction for fining the molten glass, subsequently homogenizing the molten glass through an operation such as stirring, and then molding the molten glass into a required shape through a specific molding method. An initial problem in manufacturing such a glass composition involves how complete discharge of minute air bubbles existing in the molten glass can be carried out during melting to provide homogeneous glass, in other words, how reliable fining can be conducted.

[0003] Accordingly, various methods have been studied thus far for overcoming the problem of fining. A method, which is most commonly used, involves adjusting and mixing in advance a trace additive, so-called a fining , into raw materials to be melted and deaerating fine bubbles in the molten glass through a desired chemical

reaction at high temperatures. Further, as another method which may be adopted, there is given a method of maintaining the molten glass in a reduced-pressure or vacuum environment by adjusting an external pressure of the environment itself in which the molten glass resides.

[0004] Various additives have been used as fining for the former method, and appropriate fining have been selected in response to diversification of glass materials involved in expansion of applications of the glass products. Further, various studies have been conducted on the latter method as well to develop many inventions regarding this technique.

[0005] Regarding the former method, proposed in JP 06-293523 A is a method of directly introducing a clearer into an air bubble layer of a glass melting furnace instead of mixing a clearer into raw materials in advance. Further, proposed in JP 11-035338 A is an antimony clearer replacing an existing clearer such as an arsenic (As) clearer used thus far.

[0006] On the other hand, regarding the latter method, proposed in JP 2000-128549 A is a manufacture method for glass including a sub-atmospheric pressure step in which the molten glass produced in a melting step is depressurized for sub-atmosphere. However, this method becomes feasible with use of a large-scale pressure-reducing vacuum system, posing a problem of a high equipment cost. In view of the above, JP 2000-247647 A discloses a furnace

material, used for channels of the pressure-reducing vacuum system ,formed of a prescribed electric fused refractory instead of a precious metal such as platinum. Further, JP 2001-220149 A discloses a devised structure of a bubble collector which discharges air dissolved in the glass.

[0007] Further, dating back 20 years or more, proposed in US 3,622,296 is a method of fining glass using helium gas, in which borosilicate glass is used as an object of the fining.

[0008] Of the methods described above, the former method using a fining has a problem in that stable manufacture of glass may not be necessarily sustained even when an optimal fining of a specific grade is selected at the beginning of the manufacture. This is because a grade of the glass manufactured may be at an unsatisfactory level regarding bubble holes from influences of unavoidable causes such as variation of manufacture conditions. Further, trace components are used as additives, and thus, the fining must be capable of uniformly exhibiting its effect in the molten glass by preventing segregation or the like during mixing of the raw materials.

[0009] Further, the latter method using a pressure-reducing device also requires responses to basic problems arising from theoretical restrictions of the method, even if the high equipment cost can be handled to some extent. That is, evaporation (also referred to as vaporization) of glass components from the molten glass is hardly prevented when using the pressure-reducing device.

Therefore, this method may have to be applied to limited glass applications rarely posing problems in evaporation of glass components during melting. Further, taking into account an evaporation amount of the glass components during melting, formulation of raw material components may have to be designed in advance to provide a desired glass composition. Further, sufficient attention may have to be paid on incidental facilities compared to general glass melting facilities so that the evaporated glass components are not carelessly discharged outside the glass manufacture facilities. As described above, adopting this method to the fining of the molten glass forcibly and simultaneously requires responses to various problems involved in the method. Therefore, it is not easy for glass manufacturers to adopt this method because the adoption unfavorably increases limiting conditions.

[0010] Further, US 3,622,296 discloses only the use of helium for the fining of specific borosilicate glass, but suggests nothing about glass materials which can be effectively fining with helium. Therefore, no attempt had been made on developing the method disclosed in US 3,622,296 and on applying the method to other glass products with high industrial utility value such as oxide glass.

[0011] As described above, the conventional methods are hardly satisfying an important object of glass manufacture to manufacture a homogeneous glass product without bubbles, and thus, a drastic solution is desired.

SUMMARY OF THE INVENTION

[0012] The present invention has been made in view of the above, and an object of the present invention regarding multicomponent oxide glass is therefore to provide a novel glass composition capable of drastically solving problems involved in clarification during melting.

[0013] The inventors of the present invention have found out that adjusting contents of a polyvalent element, minimum valence cations thereof, and helium in a multicomponent oxide glass composition can provide a drastic solution to the problem involved in the fining during melting and have completed the invention.

[0014] In other words, the glass composition of the present invention is characterized by containing: 10 ppm or more of at least one type of a polyvalent element; minimum valence cations of the polyvalent element in a ratio of the minimum valence cation content to the total polyvalent element content of 5 to 98% in mass ratio; and 0.01 to 2 μl/g (0°C, 1 atm) of helium.

[0015] Here, the phrase "containing 10 ppm or more of at least one type of a polyvalent element" means that a total content of the polyvalent element is 10 ppm or more, if the glass composition contains one type of polyvalent element. In addition, the phrase means that a total content of each polyvalent element is 10 ppm or more, if the glass composition contains two or more types of polyvalent elements. All or most of each polyvalent element exist

as cations having multiple valences in the glass composition. The total content of each polyvalent element refers to a sum of contents of all cations having different valences. If a part of the polyvalent element exists as atoms in the glass composition, the total content refers to a sum total of the above sum of cation contents and the content as atoms. A polyvalent element content of less than 10 ppm is not preferable for attaining an effect of the present invention to discharge bubbles in the glass. Further, generation of the bubbles in the molten glass may greatly vary depending on various external and uncertain melting conditions such as temperature and a flow rate of the molten glass. Therefore, the content of each polyvalent element is preferably 20 ppm or more for achieving more stable bubble-discharging property, considering variation in bubble generation. Further, if the glass composition contains 3 or more types of polyvalent elements, the content of at least one polyvalent element is preferably 50 ppm or more, for achieving high performance of discharging bubbles from the molten glass. Further, if a glass manufacture rate is 100 cm^3/minutes or more, the content of at least one polyvalent element is preferably 100 ppm or more. Further, if the glass product is used for applications with particularly demanding technical standards on bubble quality in the molten glass, the content of at least one polyvalent element is preferably 200 ppm or more.

[0016] Further, the term "minimum valence cations" refers to

cations, having the minimum valence, of the multiple types of cations (cations having different valences) of each polyvalent element existing in the glass composition. A ratio of the minimum valence cation content to the total content of each polyvalent element is 5 to 98% in mass ratio. In other words, if the glass composition contains one type of polyvalent element, the ratio of the minimum valence cation content to the total content of the polyvalent element is 5 to 98% in mass ratio. If the glass composition contains two or more types of polyvalent elements, the ratio of each minimum valence cation content to the total content of each polyvalent element is 5 to 98% in mass ratio.

[0017] If the ratio of the minimum valence cation content is 5% or more, a function of fining minute air bubbles existing in the molten glass is significant, allowing easy fining of air bubbles of even 1 mm or smaller. If the ratio of the minimum valence cation content is less than 5%, a sufficient function cannot be observed. The ratio of the minimum valence cation content is preferably 10% or more for a sufficiently stable fining function. Further, the ratio of the minimum valence cation content is preferably 15% or more for achieving a sufficiently stable fining effect, preferably 20% or more for achieving a more stable clarification effect, if the glass composition contains 3 or more types of polyvalent elements. On the other hand, if the ratio of the minimum valence cation content is too large, an amount of gas such as oxygen gas generated

accompanying the fining becomes too large. Thus, even if clarification of minute bubbles existing in the molten glass is attained, numerous new bubbles generate and the fining itself becomes difficult. From those views, the ratio of the minimum valence cation content in the glass composition must be 98% or less. That is, if the ratio of the minimum valence cation content exceeds 98%, problem arises in that bubbles remain in the glass products after molding. Further, for glass products required to melt at 1,300°C or more, the ratio of the minimum valence cation content is preferably 95% or less, preferably 90% or less for more assuredly achieving a stable grade of the glass products.

[0018] Further, the glass composition contains 0.01 to 2 μl/g (0°C, 1 atm) of helium in the present invention. Incorporating a prescribed amount of the helium, which is an inert gas component, in the glass composition allows complete removal or significant reduction of the air bubbles in the molten glass by discharging the air bubbles from the molten glass, thereby providing a high clarification effect for the multicomponent oxide glass composition.

[0019] The helium is not involved in network forming of a glass structure, but coexistence of the polyvalent element having such a ratio of the minimum valence cation content as described above with the helium in the glass composition provides a high fining effect. The helium content providing such an effect must be 0.01 μl/g or more in the glass composition. If the helium content is

less than 0.01 μl/g, a sufficient fining effect cannot be exhibited.

[0020] On the other hand, if the helium content in the glass composition exceeds 2 μl/g, re-foaming called reboiling may likely be observed undesirably through re-heating treatment or the like of the glass composition. A preferable upper limit of the helium content is 1.4 μl/g for inhibiting reboiling, though varying depending on the glass composition, heating conditions, or the like. The preferable upper limit of the helium content shifts to a lower value for a glass composition, in which a clearer except helium coexists, to as low as 0.9 μl/g because reboiling tends to occur more easily.

[0021] The inventors of the present invention speculate as follows on how, specifically, a satisfactory fining effect can be provided when a prescribed amount of the polyvalent element and the helium coexist in the glass composition.

[0022] The helium is often called an inert gas, a noble gas, or the like, has a stable closed shell structure, and is a monoatomic molecule. Further, the helium is the lightest element among the noble gas elements, and is also structurally very small having an atomic radius of 1.95 angstroms. An attracting force from Van der Waals force of the helium is very small, and thus, the helium does not solidify and is a liquid even at absolute zero at atmospheric pressure. The helium exists as captured in holes of a glass network structure constructed by other components in the glass composition

manufactured through high-temperature melting and cooled.

[0023] On the other hand, the elements constituting the molten glass are generally in a network state having a weak bonding force. The higher the temperature, the more vigorously each element position changes irregularly, accompanied by stretching vibration, rotation vibration, and angular vibration at relatively high speed. As described above, the helium hardly bonds with various elements constituting the molten glass and has a size enabling passing through gaps of a vibrating network as pathways. Thus, the helium is capable of easily diffusing even to bubbles existing as defects in the molten glass, without being affected by the surrounding elements.

[0024] When the polyvalent element is dissolved in such molten glass, cations of the polyvalent element in the molten glass generally are in a state where multiple types of cations having different valences exist in a specific ratio. However, coexistence with the helium in the molten glass shifts equilibrium among existence ratios of the multiple types of polyvalent element cations to a direction of increasing the amount of low valence cations. As a result, the amount of the cations having low valences increases in the molten glass while an excess gas component such as oxygen generates along with the equilibrium shift. Then, the generated gas component such as oxygen diffuses with the dissolved helium even to minute air bubbles existing in the molten glass. Thus, diameters of the minute bubbles are expanded to significantly increase a floating rate of

the minute air bubbles in the molten glass. As a result, the bubbles in the molten glass is discharged out of the glass, and thus, the fining takes place.

[0025] The "multicomponent oxide glass composition" of the present invention refers to oxide glass containing two or more types of oxides as main components and containing 50% or more as mass ratio in total of the two or more types of oxides, as main components. The "multicomponent oxide glass composition" of the present invention does not apply to a glass composition having a single composition with several components mixed as impurities. For example, the "multicomponent oxide glass composition" of the present invention does not apply to a glass composition having close to 99% in mass% of a single component such as silica and 0.09 mass% or less, two decimal places, of the several components respectively.

[0026] Further, the glass composition of the present invention preferably contains, in addition to the above components, at least one component selected from the group consisting of fluorine (F), chlorine (Cl), and sulfur trioxide (SO_3), in a mass ratio of 1 ppm or more, or a hydroxide group (OH group) in a mass ratio of 10 ppm or more.

[0027] If one component is selected from F, Cl, and SO_3, the content ratio thereof is 1 ppm or more. If two components or three components are selected therefrom, the content ratio of each component is 1 ppm or more.

[0028] Various components which may be gasified exist in the glass composition, and among them, a particularly clear effect of the present invention may be observed with F, Cl, SO_3, or the OH group. F, Cl, or SO_3 existing in a mass ratio of 1 ppm or more can enhance an effect of fining the molten glass. The OH group must exist in a mass ratio of 10 ppm or more for exhibiting the same effect as with F, Cl, and SO_3. Enhancement of the fining effect through existence of those components is presumed to result from actions of F, Cl, SO_3, or the OH group during air bubble generation in the molten glass, to suppress generation of numerous bubbles of minute diameters and to generate bubbles with as large diameters as possible.

[0029] Here, F has a function of promoting the fining by reducing viscosity of the molten glass, but is preferably incorporated in a mass ratio of 20 ppm or more for more assuredly achieving the fining function. Further, a high-viscosity glass composition melted at 1,400°C or more preferably contains 50 ppm or more of F. On the other hand, the amount of F added is preferably kept as low as possible within a range achieving the effect from environmental concerns. Further, an upper limit of the amount of F added should not exceed 0.5% in mass percent in all respects even when no environmental influences are concerned.

[0030] Further, single use of Cl has been considered to provide a fining effect of the molten glass similar to F, but the effect

of the present invention exceeds the fining effect provided using Cl independently. Addition of Cl in a mass ratio of 1 ppm or more provides homogeneous glass through assured fining even for glass considered to be hardly homogenized. Such a hardly-homogenized glass contains preferably 10 ppm or more in mass ratio of Cl added for achieving a higher clarification function, preferably 30 ppm or more thereof added for achieving highly stable clarification that is not affected by operational or furnace conditions or the like. Further, if a large amount of the helium cannot be added for various circumstances, the added helium must be definitely used for the fining. In such a case, 100 ppm or more of Cl is preferably incorporated. The hardly-homogenized glass such as no-alkali glass contains preferably 200 ppm or more of Cl added, possibly 300 ppm or more thereof added for achieving a more stable effect.

[0031] Further, SO_3 is added in the glass by employing a sulfate as a raw material and have been used for providing a fining effect from solubility of SO_3 in the molten glass being large at low temperature and being small at high temperature. However, the effect of the present invention exceeds the fining effect provided using SO_3 independently, and such an effect can be provided by adding 1 ppm or more of SO_3 in mass ratio. A glass composition with low reactivity at high temperatures contains preferably 20 ppm or more of SO_3 added, preferably 50 ppm or more thereof added for providing a more stable effect. A high-viscosity glass composition requiring

high temperature of 1,400°C or more for melting thereof preferably contains 300 ppm or more of SO_3 added.

[0032] An effect of the OH group similar to F or the like have attracted attention to reduce high-temperature viscosity of the glass, allowing easy floating of the bubbles in the molten glass. The OH group is known to possess a clarification function similar to F. However, the effect of the present invention exceeds the clarification effect of the OH group used independently, and such an effect may be provided by adding 10 ppm or more of the OH group in mass ratio. A glass composition having high high-temperature viscosity and requiring 1,200°C or more for melting thereof contains preferably 40 ppm or more of the OH group added, preferably 60 ppm or more thereof for more stably achieving the effect. Further, 100 ppm or more of the OH group may be added for cases where a sufficient addition amount of the helium cannot be ensured.

[0033] Further, in the above composition, the ratio of the content of the minimum valence cations of the polyvalent element to the polyvalent element content is preferably higher by 0.1 to 40% compared to that of a glass composition manufactured by melting in an oxygen-containing atmosphere. That is, the glass composition of the present has a relatively increased content of the minimum valence cations of the polyvalent element by the above ratio compared to the glass composition manufactured using the same glass raw materials as those of the glass composition of the present invention

under the same manufacture conditions except for the oxygen-containing atmosphere for a melting atmosphere.

[0034] Here, if the glass composition contains multiple types of polyvalent elements, the above conditions are preferably provided for each of the polyvalent elements. Further, "oxygen-containing atmosphere" refers to an atmosphere containing 1 vol% or more oxygen.

[0035] If the ratio of the minimum valence cation content is higher by less than 0.1% compared to that of the glass composition manufactured by melting in an oxygen-containing atmosphere, ability of deaerating the bubbles from the molten glass becomes small. The ratio is preferably higher by 0.3% or more, more preferably higher by 0.5% or more. If the ratio is higher by 1% or more, efficient fining can be provided for high-viscosity molten glass from which fine bubbles of about 0.1 mm are hardly eliminated. Such a ratio is particularly preferable for a glass composition requiring melting at 1,400°C or more.

[0036] On the other hand, if the ratio of the minimum valence cation content is higher by more than 40% compared to that of the glass composition manufactured by melting in an oxygen-containing atmosphere, a bubble discharging effect is undesirably reduced. Further, the ratio is preferably higher by 30% or less for the molten glass having a viscosity of 10^3 dPa·s at high temperatures of 1,000°C or more, preferably higher by 20% or less for achieving a more stable bubble discharging function.

[0037] Further, in the above composition, the glass composition preferably contains 1 ppm or more of the polyvalent element cations. If the glass composition contains multiple types of polyvalent elements, the above conditions are preferably provided for each of the polyvalent elements.

[0038] Further, the polyvalent element is preferably an element having a first ionization energy of 6 to 10 eV. An effect of promoting bubble discharge from the molten glass tends to be high apparently, particularly when the first ionization energy of the polyvalent element, the energy required for the polyvalent element to discharge an electron to become a cation, is within the above range. A reason for such has not been revealed, but the inventors of the present invention presume that when the energy required for transition to a different electronic state falls within a prescribed range, an equilibrium constant of oxidation-reduction equilibrium regarding the polyvalent element in the molten glass changes through diffusion of the helium into the molten glass. The oxidation-reduction equilibrium changes relatively, and thus, gas such as oxygen is easily discharged.

[0039] In the above composition, the polyvalent element is preferably at least one type of an element selected from the group consisting of vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), germanium (Ge), arsenic (As), selenium (Se), yttrium (Y),

zirconium (Zr), molybdenum (Mo), rhodium (Rh), silver (Ag), cadmium (Cd), tin (Sn), antimony (Sb), tellurium (Te), titanium (Ti), platinum (Pt), gold (Au), and bismuth (Bi).

[0040] The glass composition of the present invention, which is a multicomponent oxide glass composition, contains at least two types of elements which may become cations as elements constituting the glass in addition to the polyvalent element and further contains oxygen as an element which may become an anion.

[0041] Specific examples of the elements which may become cations include silicon (Si), aluminum (Al), boron (B), phosphorus (P), lead (Pb), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), lanthanum (La), lithium (Li), sodium (Na), potassium (K), gallium (Ga), and cesium (Cs). The glass composition of the present invention contains at least two types of those elements.

[0042] Further, a preferable example of the glass composition of the present invention is silicate glass containing SiO_2 within the range of 80 mass% to 30 mass%, represented by mass percentage as oxides.

[0043] Further, preferable examples of the glass composition of the present invention will be listed below, concerning applications or the like as well: a glass composition preferably containing 40 to 70% SiO_2, 5 to 25% Al_2O_3, 5 to 20% B_2O_3, and 0 to 50% RO (R = Mg + Ca + Ba + Sr + Zn) in mass percentage for no-alkali glass used in liquid crystal displays or the like, for example;

a glass composition preferably containing 45 to 70% SiO_2, 0 to 20% Al_2O_3, 0 to 55% RO (R = Mg + Ca + Ba + Sr + Zn), and 0 to 5% B_2O_3 for sheet glass used in flat panel displays except liquid crystal displays, for example; a glass composition preferably containing 50 to 80% SiO_2, 10 to 35% Al_2O_3, 1 to 10% Li_2O, and 0 to 39% RO (R = Mg + Ca + Ba + Sr + Zn) for crystallized glass used in building materials, cooking utensils, optical parts, or the like, for example; a glass composition preferably containing 40 to 70% SiO_2, 0.1 to 20% Al_2O_3, 5 to 20% B_2O_3, and 0 to 55% RO (R = Mg + Ca + Ba + Sr + Zn) for glass used in sheet glass for optical semiconductor case and packaging applications and optical parts such as lenses, for example; and a glass composition preferably containing 50 to 70% SiO_2, 0.1 to 25% Al_2O_3, and 0.5 to 30% RO (R = Mg + Ca + Ba + Sr + Zn) for glass fiber used in a printed-wiring assembly or a composite mixed with concrete, for example.

[0044] If Sn is selected as the polyvalent element, a ratio of a divalent cation content of Sn to the total Sn content is preferably 20 to 50%, more preferably 20 to 45%, further more preferably 26 to 40% in mass ratio.

[0045] Here, Sn cations existing in the molten glass are Sn^{2+} (divalent cation) and Sn^{4+} (tetravalent cation), and the minimum valence cation of Sn is Sn^{2+}. The total Sn content, following the criteria described above, is the sum of Sn^{2+} and Sn^{4+} contents, or the sum total of the above sum of the cation contents and the Sn

content if a part of Sn exists as Sn atoms in the glass composition. Sn is often used in manufacture of sheet glass, in refractive index adjustment of optical glass, or the like. More preferable results can be provided by restricting the ratio of the Sn^{2+} content within the above range, Sn^{2+} being the minimum valence cation of Sn.

[0046] Further, if Sb is selected as the polyvalent element, a ratio of a trivalent cation content of Sb to the total Sb content is preferably 70% or more, more preferably 80% or more, further more preferably 91% or more in mass ratio.

[0047] Here, Sb cations existing in the molten glass are Sb^{3+} (trivalent cation) and Sb^{5+} (pentavalent cation), and the minimum valence cation of Sb is Sb^{3+}. The total Sb content, following the criteria described above, is the sum of Sb^{3+} and Sb^{5+} contents, or the sum total of the above sum of the cation contents and the Sb content if a part of Sb exists as Sb atoms in the glass composition. Sb is often used as a clearer for the molten glass, and more preferable results can be provided by restricting the ratio of the Sb^{3+} content within the above range, Sb^{3+} being the minimum valence cation of Sb.

[0048] Further, if As is selected as the polyvalent element, a ratio of a trivalent cation content of As to the total As content is preferably 60% or more, more preferably 70% or more in mass ratio.

[0049] Here, As cations existing in the molten glass are As^{3+} (trivalent cation) and As^{5+} (pentavalent cation), and the minimum

valence cation of As is As^{3+}. The total As content, following the criteria described above, is the sum of As^{3+} and As^{5+} contents, or the sum total of the above sum of the cation contents and the As content if a part of As exists as As atoms in the glass composition. As is used as a clearer for the molten glass similar to Sb. More preferable results can be provided by restricting the ratio of the As^{3+} content within the above range, As^{3+} being the minimum valence cation of As.

[0050] Further, if Fe is selected as the polyvalent element, a ratio of a divalent cation content of Fe to the total Fe content is preferably 30% or more, more preferably 40% or more in mass ratio.

[0051] Here, Fe cations existing in the molten glass are Fe^{2+} (divalent cation) and Fe^{3+} (trivalent cation), and the minimum valence cation of Fe is Fe^{2+}. The total Fe content, following the criteria described above, is the sum of Fe^{2+} and Fe^{3+} contents, or the sum total of the above sum of the cation contents and the Fe content if a part of Fe exists as Fe atoms in the glass composition. Fe is added to the glass for purposes such as glass coloring and enhancing infrared absorption ability or is mixed into the glass by employing a silica or alumina raw material or the like of not high-purity. More preferable results can be provided by restricting the ratio of the Fe^{2+} content within the above range, Fe^{2+} being the minimum valence cation of Fe.

[0052] Further, the glass composition of the present invention

can appropriately contain: colorants such as other transition metal compounds, tellurium compounds, selenium compounds, rare earths, and sulfides exhibiting color with various colored ions, additives causing colloid coloring such as a CdS-CdSe solid solution, and radiation coloring additives such as Ce; and additives of scarce metal elements for adjusting transmittance or refractive index. Further, in contrast, elements such as U, Th, Pb, Ra, and K may be finely controlled as appropriate to a ppm order or a ppb order to allow melting of the glass so that the molten glass contains a minimal amount of the elements, to deal with demands from applications employing the glass composition.

[0053] Further, the glass composition of the present invention can respond to various manufacture conditions according to applications including: ion exchange treatment for imparting desired properties such as strength property and optical property; provision of various thin films to a glass surface; implantation of specific ion species to the glass surface; glass surface treatment with chemicals for improving surface property of the glass or the like; solidification of radioactive substances or toxic substances; rapid-quenching vitrification and molding using liquid nitrogen, liquid helium, or the like; glass manufacture by ultra-high temperature melting using solar energy or the like; special glass manufacture using a phenomenon of crystallization or the like under ultra-high pressure conditions; and inclusion of specific additives

for imparting other special electromagnetic properties to the glass.

[0054] Further, an example of the raw materials which can be used for manufacturing the glass composition of the present invention includes materials containing: a single substance, a mixture, or a compound of inorganic substances such as oxides, carbonates, phosphates, chlorides, and various glass as a main component; and a single substance, a mixture, or a compound of organic additives, metal additives, or the like in addition to the above various inorganic substances as an additive. Classification of the glass based on source of glass materials such as natural products, synthetic products, or purified products does not matter. Further, highly purified industrial products, with impurities in a ppm order or a ppb order removed through various methods, can be employed as raw materials of the glass composition of the present invention. Further, general raw materials for glass manufacture, manufactured and purified in mining and chemical industry and used, may also be used as raw materials of the glass composition of the present invention.

[0055] Further, melting of the glass raw materials generally involves: collectively maintaining the glass raw materials in a heat-resistant container of ceramics, platinum, or the like as while supplying energy from a heat source such as electricity or gas; and then melting the materials while preventing the multiple raw materials from separating during high-temperature heating. However,

methods which may be employed as appropriate include: applying external force such as current pressure and electromagnetic force; and floating the molten glass above the liquid metal.

[0056] (1) As described above, a glass composition of the present invention contains: 10 ppm or more of at least one type of a polyvalent element; minimum valence cations of the polyvalent element in a ratio of the minimum valence cation content to total content of the polyvalent element of 5 to 98% in mass ratio; and 0.01 to 2 μl/g (0°C, 1 atm) of helium in a multicomponent oxide glass composition, allowing discharge of minute air bubbles existing in molten glass from the molten glass by rapidly expanding diameters of the bubbles during melting. Therefore, homogeneous glass products with reduced or no bubble defects can be manufactured by achieving a satisfactory fining effect during melting even with glass materials which have been conventionally hardly melted and manufactured into homogeneous glass products.

[0057] (2) A fining effect of molten glass may be further enhanced with a glass composition containing, in addition to the above components, 1 ppm or more of at least one component selected from the group consisting of F, Cl, and SO_3, and/or 10 ppm or more of OH in mass ratio.

[0058] (3) Further, a stable and efficient clarification effect can be achieved with a glass composition having a higher ratio of the minimum valence cation content by 0.1 to 40% compared to that

of a composition manufactured by melting in an oxygen-containing atmosphere or incorporating 1 ppm or more of polyvalent cations in the glass composition.

[0059] (4) Selecting at least one type of an element, as a polyvalent element, from the group consisting of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Y, Zr, Mo, Rh, Ag, Cd, Sn, Sb, Te, Ti, Pt, Au, and Bi allows the selected polyvalent element to contribute to glass coloring and to an improvement in chemical durability, in addition to the clarification effect. Further, the selected polyvalent element can impart various functions of high levels to the glass composition, in addition to homogeneity.

[0060] (5) In particular, selecting Sn, Sb, As, or Fe as a polyvalent element and adjusting a ratio of a minimum valence cation content to a total content of each of those elements within a specific range allows more preferable results regarding fining.

DETAILED DESCRIPTION OF THE INVENTION

[0061] Hereinafter, the glass composition of the present invention will be described in detail by way of examples.

[0062] [Example 1] The inventors of the present invention have conducted a research following a procedure described below to confirm fining performance of a glass composition of the present invention. First, Table 1 shows the researched glass compositions. In Table 1, reference symbol A represents no-alkali glass with poor melting

property, and reference symbol B represents glass with excellent melting property, containing relatively high amounts of alkali metal elements. Reagent grade, high purity glass raw materials were selected to yield the glass compositions shown in Table 1, and preliminary analysis confirmed that the amounts of impurities or the like can be sufficiently grasped as well. The raw materials were weighed and then subjected to mixing for 1 hour using a rotary raw material mixer, to thereby prepare a raw material batch subjected to sufficient mixing. Then, the raw material batch was charged into a platinum-rhodium crucible. The crucible was placed in an indirect electric resistance furnace maintained at a prescribed temperature, and then maintained at 1,550°C for 2 hours, to thereby cause a vitrification reaction. The batch was subjected to 4 more hours of melting while adjusting a helium content in the glass by introducing helium, gas adjusted to 50 to 99.9% concentration with nitrogen, into the furnace through a gas supply pipe.

[0063] Subsequently, molten glass was cooled to room temperature inside the furnace slowly cooled, and investigations were conducted by gathering samples required for determination of the number of bubbles in the glass obtained, for analysis of helium (He) gas in the glass, and for analysis of the polyvalent elements. Determination of the number of bubbles involved both visual observation and observation using a microscope of 20 power magnification. Further, helium gas was analyzed using a quadrupole

mass spectrometer (QMA125, manufactured by Balzers AG) installing a secondary electron multiplier (SEM) for improving measurement sensitivity. Gas analysis using the quadrupole mass spectrometer involved: placing a required amount of glass sample to be measured in a platinum dish, keeping the platinum dish in a sample chamber to vacuum of 10^{-5} Pa (that is, 10^{-8} Torr); and introducing the gas heated and discharged into the quadrupole mass spectrometer having a measuring sensitivity of 0.001 μl/g.

[0064] Further, valences of the polyvalent elements in the glass were analyzed using necessary analyzers or the like after the obtained glass was decomposed with an acid or dissolved in an alkali. Sn and Sn^{2+} were analyzed through the following mode, for example. Part of a glass block cooled was used for chemical analysis to determine the total amount of existing Sn and Sn^{2+}. The total amount of existing Sn and Sn^{2+} was determined through instrumental analysis and redox titration after the glass was decomposed in an acidic solution. Further, an amount of Sn^{2+} was indirectly determined by titrating the amount of Fe^{2+}, formed from reduction by Sn^{2+} in the decomposed solution, with a cerium sulfate solution. To be specific, the total amount of Sn was determined by preparing a sample solution through heat decomposition of glass powder with sulfuric acid and hydrofluoric acid and subsequent dissolution of the decomposed glass powder in hydrochloric acid and by using an ICP-AES device. Sn^{2+} was heat decomposed for 10 minutes (in water bath) in an inert gas

environment by first adding 2 ml of a 0.1% Fe^{3+} solution to the glass powder and then adding the sulfuric acid and the hydrofluoric acid thereto. During the heat decomposition, Fe^{3+} was reduced by Sn^{2+} to form Fe^{2+}. Subsequently, boric acid was added to the resultant solution to neutralize the excess hydrofluoric acid, and then introduction of the inert gas was stopped. Then, 1 ml of a 0.015 M OsO_4 solution was added to the resultant solution as a catalyst of the present invention, and 1.0 ml of an o-phenanthroline indicator was added. Sn^{2+} was analyzed and an amount thereof was determined through indirect titration involving titrating with a 1/200 N cerium sulfate solution until color of the solution changed from orange to pale blue.

[0065]

[Table 1]

Glass name / Components (mass%)	A	B
SiO_2	59.0	61.5
Al_2O_3	16.3	2.1
B_2O_3	9.0	–
CaO	5.3	–
SrO	6.1	9.0
BaO	3.1	9.7
ZnO	1.0	0.5
Na_2O	–	7.5
K_2O	–	7.5
TiO_2	–	0.6
ZrO_2	0.2	1.6

[0066] Table 2 shows the obtained results. Glass types in Table 2 correspond to glass names in Table 1. As shown in Table 2, glass

were prepared by adding 1.0% in mass ratio of As, Sb, or Sn as an oxide of the polyvalent element and adjusting a ratio of the minimum valence cation content to the polyvalent element content. In samples 1 to 9, the number of bubbles in the glass after melting was 1 to 136 bubbles per 10 g of glass.

[0067]

[Table 2]

Sample	1	2	3	4	5	6	7	8	9
Glass type	A	A	A	A	A	A	A	A	A
Type of polyvalent element oxide	As_2O_3	As_2O_3	As_2O_3	Sb_2O_3	Sb_2O_3	Sb_2O_3	SnO_2	SnO_2	SnO_2
Amount of polyvalent element oxide added (mass%)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
(Amount of minimum valence cations)/(amount of polyvalent elements) x 100	75	77	80	91	92	96	27	28	29
He content (µl/g-glass : 0°C, 1 atm)	0.01	0.02	0.05	0.01	0.04	0.05	0.02	0.04	0.07
Number of bubbles (bubbles/10 g-glass)	15	9	1	136	120	70	31	20	1

[0068] [Comparative Example 1] Melting was conducted following a similar procedure as in Example 1 and using the same device as in Example 1, except that the melting was conducted in

air for 4 hours instead of in helium for 4 hours in the final step as in Example 1 (step of melting while introducing helium). Table 3 shows the results.

[0069]

[Table 3]

Sample	10	11	12
Glass type	A	A	A
Type of polyvalent element oxide	As_2O_3	Sb_2O_3	SnO_2
Amount of polyvalent element oxide added (mass%)	1.0	1.0	1.0
(Amount of minimum valence cations)/(amount of polyvalent elements) x 100	72	90	26
He content (μl/g-glass: 0°C, 1 atm)	<0.01	<0.01	<0.01
Number of bubbles (bubbles/10 g-glass)	46	182	115

[0070] As (arsenic), which is the same polyvalent element as in the samples 1, 2, and 3 (Example 1) in Table 2, was used for the sample 10 (Comparative Example 1) in Table 3. Sb (antimony), which is the same polyvalent element as in the samples 4, 5, and 6 (Example 1) in Table 2, was used for the sample 11 (Comparative Example 1) in Table 3. Sn (tin), which is the same polyvalent element as in the samples 7, 8, and 9 (Example 1) in Table 2, was used for the sample 12 (Comparative Example 1) in Table 3. However, comparing the samples of Example 1 and Comparative Example 1 by the types of polyvalent elements added confirmed that the number of bubbles in the glass in Example 1 was significantly reduced compared to

the glass in Comparative Example 1. Further, analysis of the helium content in the glass in Comparative Example 1 (samples 10 to 12) resulted in a low value of less than 0.01 μl/g, probably mixed from air or the like.

[0071] Further, As^{3+} content ratios (ratios of As^{3+} contents to total As contents) of the samples 1, 2, and 3 (Example 1) in Table 2 were respectively 75%, 77%, and 80% in mass ratio, As^{3+} being the minimum valence cation of As. Those values were higher by 3%, 5%, and 8% compared to the As^{3+} content ratio of the sample 10 in Table 3 of 72%. Similarly, Sb^{3+} content ratios (ratios of Sb^{3+} contents to total Sb contents) of the samples 4, 5, and 6 (Example 1) in Table 2 were respectively 91%, 92%, and 96% in mass ratio, Sb^{3+} being the minimum valence cation of Sb. Those values were higher by 1%, 2%, and 6% compared to the Sb^{3+} content ratio of the sample 11 in Table 3 of 90%. Further, Sn^{2+} content ratios (ratios of Sn^{2+} contents to total Sn contents) of the samples 7, 8, and 9 (Example 1) in Table 2 were respectively 27%, 28%, and 29% in mass ratio, Sn^{2+} being the minimum valence cation of Sn. Those values were higher by 1%, 2%, and 3% compared to the Sn^{2+} content ratio of the sample 12 in Table 3 of 26%.

[0072] [Example 2] Melting was conducted following a similar procedure as in Example 1, using the same device as in Example 1 and using glass raw materials containing sulfates, chlorides, and hydroxides so that amounts of SO_3, Cl, and OH added could be changed.

Table 4 shows the results.

[0073]

[Table 4]

Sample	13	14	15	16		17		18	
Glass type	B	B	B	A		A		A	
Type of component added	SO_3	SO_3	SO_3	Cl	OH	Cl	OH	Cl	OH
Content of component added in glass (mass%)	0.14	0.12	0.05	0.16	0.014	0.15	0.012	0.13	0.006
He content (µl/g-glass: 0°C, 1 atm)	0.01	0.03	0.07	0.01		0.04		0.06	
Number of bubbles (bubbles/10 g-glass)	4	2	1	47		28		16	

[0074] The samples 13, 14, and 15 were glass containing sulfates, as raw materials, added to glass B shown in Table 1, providing homogeneous glass with a very little number of bubbles in the glass. Further, the samples 16, 17, and 18 were glass containing chlorides and hydroxides, as raw materials, added to glass A shown in Table 1, providing glass with 16 to 47 bubbles per 10 g of glass, which is a sufficiently small number of bubbles in the glass.

[0075] [Comparative Example 2] Melting was conducted following a similar procedure as in Example 2 and using the same device as in Example 2, except that the melting was conducted in air for 4 hours instead of in helium for 4 hours in the final step as in Example 2 (step of melting while introducing helium). Table 5 shows the results.

[0076]

[Table 5]

Sample	19	20	
Glass type	B	A	
Type of component added	SO_3	Cl	OH
Content of component added (mass%) in glass	0.20	0.17	0.019
He content (μl/g-glass: 0°C, 1 atm)	<0.01	<0.01	
Number of bubbles (bubbles/10 g-glass)	10	145	

[0077] The sample 19 (Comparative Example 2) in Table 5 was glass containing SO_3 added to glass B, similar to the samples 13, 14, and 15 (Example 2) in Table 4, providing glass with a larger number of bubbles compared to the samples 13, 14, and 15 because helium was not introduced. Further, the sample 20 (Comparative Example 2) of Table 5 was glass containing Cl or OH added to glass A, similar to the samples 16, 17, and 18 (Example 2) in Table 4, providing glass with a significantly larger number of bubbles, 145 bubbles per 10 g of glass, compared to the samples 16, 17, and 18 because helium was not introduced.

[0078] [Example 3] Based on the above results, the inventors of the present invention have attempted to introduce the helium gas into an actual continuous melting furnace manufacturing a glass product shown in Table 6, to thereby improve the bubble quality. The glass product shown in Table 6 is used for image display devices

such as liquid crystal displays.

[0079]

[Table 6]

(mass%)

Glass name	SiO_2	Al_2O_3	MgO	Li_2O	Na_2O	K_2O	P_2O_5	ZrO_2	TiO_2	As_2O_3
C	65.8	22.3	0.6	4.1	0.6	0.4	1.4	2.3	2.0	0.5

[0080] The melting furnace used for manufacturing the above glass product is a tank melting furnace provided with a first melting chamber, a second melting chamber, and a fining chamber. The furnace is provided with two heat sources of gas firing and electrodes. The furnace has a maximum melting temperature of 1,600°C and requires 48 hours of residence time for the molten glass. The helium was introduced from hearth of the first melting chamber through a heat-resistant gas introducing pipe into the molten glass at 30 l/minutes. The fining effect of and dissolved components in the glass manufactured as above were analyzed. As a result, 0.08 μl/g of helium was dissolved in the glass, and a ratio of the minimum valence cation (As^{3+}) content to the total As content was 76% in mass ratio. In addition, the glass had 1 air bubble/kg glass, and enhanced homogeneity and improved efficiency percentage by 1.2% compared to conventional products.